Cure Kinetics of DGEBA/MDA System with Various Contents of NPG

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NPG 함량에 따른 DGEBA/MDA 계의 경화반응 속도론

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Abstract The isothermal cure behavior of diglycidyl ether of bis phenol A(DGEBA)/4,4'-methylenedianiline(MDA) system with various content of neopentyl glycol(NPG) has been analyzed by differential scanning calorimetry(DSC). To increase the cure rate of DGEBA/MDA system, NPG was introduced as an accelerator. Regardless of the NPG content, the shape of the conversion curves showed sigmoid indicating that DGEBA/MDA/NPG system followed autocatalytic cure reaction. The cure reaction of DGEBA/MDA system increased with the increment of NPG content and it was due to the catalytic role of hydroxyl groups of NPG.

1. Introduction

It has been well known that there are many catalysts such as -OH, -COOH, -SO3H and CONH2 which can donate hydrogen bonds to the amine–epoxide reaction. In this study, the catalytic effect of hydroxyl groups was investigated. To increase the cure rate of epoxy system, neopentyl glycol (NPG) was added.

It has been well known that the cure rate of epoxy/diamine system is expressed by the multiplication of noncatalytic reaction and autocatalytic reaction as follows (1-11)

\[ \dot{\alpha} = \frac{d\alpha}{dt} = (k_1 + k_2\alpha^m) (1 - \alpha)^n \]  

where, \( \dot{\alpha} \) : cure rate, \( \alpha \) : degree of cure, \( k_1 \) \& \( k_2 \) : rate constants and \( m \) \& \( n \) : reaction orders. \( k_1 \) represents the rate constant associated with noncatalytic reaction between epoxide group and amine group and also associated with the catalytic reaction due to the existence of catalyst in the initial formulation. \( k_2 \) represents the rate constant associated with the autocatalysis by the hydroxyl groups generated from the reaction between epoxide group and amine group. From the first assumption that the initial cure rate was not zero, \( k_1 \) was the same value of \( \dot{\alpha} \) at \( t=0 \), which can be readily obtained from the DSC curve and it is

\[ k_1 = \dot{\alpha}_0 = \left( \frac{d\alpha}{dt} \right)_{t=0} \]  

To get other kinetic parameters, the following equations were used.

\[ m + n = 2 \]  

\[ \ln \left( \frac{\dot{\alpha}/(1 - \alpha)^{n-1} - k_1}{m - 2\alpha} \right) \ln \alpha = 0 \]  

\[ k_2 = -\frac{(2 - m)k_1}{m - 2\alpha} \]  

where, \( \alpha_0 \) : degree of cure at maximum peak and \( \dot{\alpha}_0 \) : cure rate at maximum peak, \( \alpha \) and \( \dot{\alpha} \) were easily obtained from the isothermal DSC curve.

2. Experiment

Diglycidylether of bisphenol A (DGEBA, Epon828) was a commercial epoxy resin supplied by Shell Co. and curing agent was 4,4'-methylenedianiline (MDA) of Fluka Chemie AG. As a catalyst, neopentyl glycol
Table 1. Temperature Dependence of Cure Kinetics Variables for DGEBA/MDA/NPG(10 phr) System.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$\dot{\alpha}_t \times 10^6$</th>
<th>$\alpha_0$</th>
<th>m</th>
<th>n</th>
<th>$k_1 \times 10^3$ (min$^{-1}$)</th>
<th>$k_2 \times 10^2$ (min$^{-1}$)</th>
<th>$E_a$ (kcal/mol)</th>
<th>A (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1.76</td>
<td>0.26</td>
<td>0.80</td>
<td>1.20</td>
<td>1.20</td>
<td>3.92</td>
<td>4.61</td>
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</tr>
<tr>
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<td>2.62</td>
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<td>0.72</td>
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<td>12.4</td>
</tr>
<tr>
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<td>0.61</td>
<td>1.39</td>
<td>1.78</td>
<td>8.90</td>
<td>22.2$\times$10$^4$</td>
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</tr>
<tr>
<td>110</td>
<td>5.51</td>
<td>0.21</td>
<td>0.52</td>
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</tr>
<tr>
<td>120</td>
<td>8.18</td>
<td>0.20</td>
<td>0.48</td>
<td>1.52</td>
<td>2.37</td>
<td>18.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(NPG) was used. Firstly, various contents of NPG melted in DGEBA at 100°C and 30 phr of MDA was added at 80°C and stored at -13°C to prevent the cure reaction during the storage. Isothermal experiment was conducted at 80°C, 90°C, 100°C, 110°C and 120°C in order to obtain both the cure rate and extent of cure as a function of time. The isothermal baseline was established at the pre-selected cure temperature and range setting by using a fully-cured sample. To get total heat, $Q_T$ evolved during the complete cure, dynamic DSC analysis was carried out from 30°C to 350°C at the heating rate of 10°C/min. The degree of conversion is

$$\dot{\alpha} = \frac{d\alpha}{dt} = \frac{1}{Q_T} \frac{dQ}{dt}$$

3. Results and Discussion

Fig. 1 shows that isothermal cure rate curves for DGEBA/MDA/NPG(10 phr) at three different temperatures. With the increment of cure temperature, the cure reaction is accelerated at the early stage of cure, maximum exothermic peak temperature appeared at shorter time and the value was increased and felled down rapidly to the baseline after maximum cure rate. When $\alpha = 0$ at $t = 0$, the Eq. (1) became Eq. (2), and this equation indicated that kinetic rate constant $k_r$ was the initial cure rate. Values of $k_r$ at different cure tempera-

Fig. 2. Kinetic constants $k_1$ and $k_2$ as a function of reciprocal curing temperature for DGEBA/MDA/NPG(10 phr).

tures were obtained from the isothermal cure rate curves and were listed on Table 1. As the increment of cure temperature, $k_r$ was increased. The relationship between cumulative heat at a time, Q and the total exothermic heat, $Q_T$ gave the conversion, $\alpha$ as a function of time, which was also plotted in Fig. 1. The sigmoid shape of the curves meant that the cure reaction of the system followed autocatalytic mechanism.

To get $m$, $n$ and $k_r$, $\alpha$ and $\dot{\alpha}$ were also listed on Table 1 and they were introduced to Eqs. (3~5). The values of kinetic parameters were also listed on Table 1.

To get activation energy and pre-exponential factor for $k_1$ and $k_2$, Arrhenius equation was used and Arrhenius plots in Fig. 2 were expressed as follows.

$$\ln k_1 = 2.17 - 2.32 \times 10^3/T$$
$$\ln k_2 = 12.3 - 5.48 \times 10^3/T$$

The activation energy was calculated from the slope and pre-exponential factor was obtained from intercept. The activation energy and pre-exponential factor for $k_1$ were 4.61 kcal/mol and 8.76 min$^{-1}$ and those values for $k_2$ were 10.89 kcal/mol and 2.22$\times$10$^5$ min$^{-1}$. A s
explained above, $k_f$ for the autocatalytic mechanism was higher than $k_i$ for the noncatalytic mechanism.

Fig. 3 shows isothermal cure rate curves for DGEBA/MDA system with various contents of NPG at three different cure temperatures. Values of $k_f$ for various contents of NPG at different cure temperatures were also obtained from the isothermal cure rate curves and were listed on Table 2. $k_f$ was increased with the increment of cure temperature and NPG content. It can be clearly explained by the role of two hydroxyl groups in NPG acting as a catalyst for DGEBA/MDA system. Conversion vs. time for the systems with various contents of NPG were obtained from the relationship between $Q$ and $Q_f$ for each system and were also shown in Fig. 3. All systems showed sigmoid shape and this meant that the cure reactions of the systems followed autocatalytic mechanism regardless of NPG content.

$m$, $n$, $k_i$, $\alpha$ and $\dot{\alpha}$ listed on Table 2 were obtained from Fig. 3, and were introduced to Eqs.(3~5). The values of kinetic parameters were also listed on Table 2.
Table 2. Temperature Dependence of Cure Kinetics Variables for DGEBA/MDA/NPG System with Various NPG Content.

<table>
<thead>
<tr>
<th>NPG Content (phr)</th>
<th>Temp. (°C)</th>
<th>( \dot{\alpha} \times 10^3 )</th>
<th>( \alpha )</th>
<th>m</th>
<th>n</th>
<th>( k_1 \times 10^3 ) (min(^{-1}))</th>
<th>( k_2 \times 10^3 ) (min(^{-1}))</th>
<th>( E_a ) (kcal/mol)</th>
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</table>

The rate constants \( k_1 \) and \( k_2 \) for every system follow Arrhenius behavior as shown in Fig. 4. Activation energy and pre-exponential factor were obtained from the slope and intercept and those values are shown in Table 2. As explained above, all systems showed that \( k_2 \) was higher than \( k_1 \). \( k_1 \) and \( k_2 \) were increased with the increment of NPG content. These results gave a good account for the catalytic role of hydroxyl groups which were added or generated. The role of hydroxyl group as a catalyst has been well known. Water, isopropanol and phenol which have hydroxyl group can act as a catalyst. Hydrogen atom of hydroxyl group and oxygen of the epoxide formed a hydrogen bond, followed by the epoxide ring opening via a termolecular transition state, and it was found that the hydroxyl group in NPG could act as a catalyst in the reaction between amine group of MDA and epoxide group in DGEBA.

The degree of cure at the peak, \( \alpha_p \) was plotted against curing temperature in Fig. 5. For a given formulation, \( \alpha_p \) decreased with the increment of the curing temperature. At any given temperature, the value, \( \alpha_p \) decreased with the increment of the content of NPG. Fig. 5 also showed that the shift of \( \alpha_p \) was decreased with the increment of NPG content. It meant that with the increment of NPG content, the effect of two hydroxyl groups of NPG was higher than that of the hydroxyl group from DGEBA/MDA. Maximum rate of cure occurs at 20~45% epoxy conversion in the temperature range examined, even though the autocatalyzed reactions were generally characterized by the maximum rate at approximately 30~40% epoxy conversion.

The reaction time required to attain this maximum rate, \( t_r \) was plotted against curing temperature in Fig. 6 and it was shown that the increment of temperature made the time required to reach the peak, \( t_r \) decreased in all systems and \( t_r \) was decreased with the increment of NPG content in the same temperature. It was good evidence that two hydroxyl of groups NPG acted as catalyst in the DGEBA/MDA system.

4. Conclusions

Regardless of the NPG content, the shape of the conversion curves showed sigmoid indicating that DGEBA/MDA/NPG system followed autocatalytic cure reaction. The kinetic constant with noncatalytic reaction, \( k_1 \) was increased with the increment of NPG content, and this was the effect of catalytic role of NPG. The kinetic constant for autocatalytic reaction, \( k_2 \) was also increased with the increment of NPG content. \( k_2 \) was larger than \( k_1 \), and \( \alpha_p \) and \( t_r \) were decreased with the increment of NPG content.
Fig. 4. Kinetic constants $k_1$ and $k_2$ as a function of reciprocal curing temperature for DGEBA/MDA system with different contents of NPG. (A) 0 phr, (B) 5 phr, (C) 15 phr and (D) 20 phr.

Fig. 5. Variation of cure degree at the peak point, $\alpha_p$, with temperature.

Fig. 6. Variation of time at the peak point, $t_p$, with temperature.
References

2. C. Domenici, G. Levita, A. Marchetti and V. Frosini, ibid., 34, 2285 (1987)